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Olivine LiCoPO₄ phase grown LiCoO₂ cathode material for high density Li batteries

Hyunjung Lee^a, Min Gyu Kim^b, Jaephil Cho^{a,*}

^a Department of Applied Chemistry, Kumoh National Institute of Technology, Gumi, Republic of Korea

^b Beamline Research Division, Pohang Accelerator Laboratory, Pohang University of Science and Technology, Pohang, Republic of Korea

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Abstract

Olivine LiCoPO₄ phase grown LiCoO₂ cathode material was prepared by mixing precipitated Co₃(PO₄)₂ nanoparticles and LiCoO₂ powders in distilled water, followed by drying and annealing at 120 °C and 700 °C, respectively, for 5 h. As opposed to ZrO₂ or AlPO₄ coatings that showed a clearly distinguishable coating layer from the bulk materials, $Co_3(PO_4)_2$ nanoparticles were completely diffused into the surface of the LiCoO₂ and reacted with lithium of LiCoO₂. An olivine LiCoPO₄ phase was grown on the surface of the bulk LiCoO₂, with a thickness of ~7 nm. The electrochemical properties of the LiCoO₄ phase, grown in LiCoO₂, had excellent cycle life performance and higher working voltages at a 1C rate than the bare sample. More importantly, Li-ion cells, containing olivine LiCoPO₄, grown in LiCoO₂ at 4.4 V, whereas those containing bare sample showed a 200% increase during storage at 90 °C for 5 h. In addition, nail penetration test results of the cell containing olivine LiCoPO₄, grown in LiCoO₂ showed a burnt-off cell pouch with a temperature above 500 °C.

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1. Introduction

Since the cylindrical 18650R-type Li-ion cell, with a capacity of 1200 mAh, was first developed in 1991, its capacity has increased by about 7–10% every year, and a 2600 mAh (500 mAh/cc) cell was developed in 2005 [1]. However, such a capacity achievement was possible only by maximum utilizing the cell dead space, modifying the thickness of the current collectors, and decreasing the amounts of binder and conducting agent in the electrodes. As of yet, the cathode material, LiCoO_2 , has remained unchanged due to its high electrode density (3.7 g/cc) and good electrochemical properties at 4.3 V. However, achieving capacities beyond 2600 mAh (e.g. 2800 mAh

(550 mAh/cc) requires an increase in the cut-off voltage of the cell from 4.2 V to 4.4 V (vs. graphite). As an alternative, we can consider new cathode materials for replacing LiCoO₂ and Ni-rich cathode materials with a specific capacity as high as 185 mAh/g [2–6]. However, the hardware of portable electronics, such as cellular phones and note-PCs, still require average working voltages above 3.7 V even in the pulse mode. In this regard, Ni-based cathode materials (electrode density, 3.4 g/cc) cannot be used.

A problem with LiCoO₂ is that, when the cut-off voltage increases to 4.5 V from 4.3 V (vs. lithium metal), the x in Li_xCoO_2 decreased from 0.45 to 0.3, resulting in a large anisotropic volume change of over 3% due to the phase transition between hexagonal, monoclinic, and H1-3 phases [7,8]. Furthermore, highly oxidized Co⁴⁺ ions are apt to decompose electrolytes in the particle surface, resulting in substantial amounts of gas generation. In addition, Co dissolution at 4.5 V at elevated temperatures induces

^{*} Corresponding author. Tel.: +82 54 467 7824; fax: +82 54 467 7710. *E-mail address:* jpcho@kumoh.ac.kr (J. Cho).

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the simultaneous Li dissolution from the cathode surface. Accordingly, this results in Li ion intercalation sites which, in turn, increase structural degradation. In order to address these problems, metal oxide and AlPO₄ coatings have been suggested [9–14], but ZrO₂ and Al₂O₃ coatings caused explosions during thermal abuse tests, such as the nail penetration test [15–17]. On the other hand, nanoparticle coatings, such as AlPO₄ coatings, have raised concerns about possible Li dissolution from LiCoO₂ during the coating procedure due to the use of water as a solvent [18]. Hence, during heat-treatment at 700 °C, Li sources co-precipitated as forms of LiOH and Li₂CO₃ on the coating layers. Since these impurity phases do not react with AlPO₄ at 700 °C and can reside on the coating layers, they eventually lead to swelling during storage at 90 °C.

In this study, we report a new coating material that reacts with lithium, resulting in the formation of a LiCoPO_4 phase, grown in the bulk LiCoO_2 . The olivine LiCoPO_4 phase is very electrochemically and thermally stable even after full delithation [19]. Accordingly, an olivine LiCoPO_4 phase, grown in the surface of the LiCoO_2 cathode material, can significantly reduce cell swelling at 90 °C at 4.4 V and also enhance the electrochemical performance.

2. Experimental section

Cobalt nitrate $(Co(NO_3)_3 \cdot 9H_2O, 1 \text{ g})$ and diammonium hydrogen phosphate $((NH_4)_2HPO_4, 0.38 \text{ g})$ were dissolved in distilled water and mechanically mixed until a white-colored, $Co_3(PO_4)_2$ nanoparticle-dispersed solution was observed. The solution was mixed with LiCoO₂ (with an average particle size of ~10 µm and BET surface area of $0.4 \text{ m}^2/\text{g}$), followed by drying at 120 °C for 5 h and annealing at 700 °C for 5 h. The estimated $Co_3(PO_4)_2$ content in the powder was 0.9 wt%.

For the 4.4 V nail penetration and swelling tests at 90 °C, the Li-ion cells with an 840 mAh standard capacity [cell size: $4.6 \times 34 \times 50 \text{ mm}^3$ (thickness × length × width)] were used. Bare and LiCoPO₄ phases, formed in the $LiCoO_2$, were used as the cathode, and the anode material was synthetic graphite. For assembling the Li-ion cells, we used 2 kg each of samples A and B for cell manufacturing. For swelling and nail penetration tests, 4 to 5 cells of each were used. The cell surface temperature was monitored, using a K-type thermocouple, placed on the center of the largest face in the cell pouch, and the thermocouple was tightly glued with an insulating tape. For the nail penetration test, a nail with a diameter of 2 mm was used, and the cell voltage was fixed at 4.4 V. Coin-type half-cell tests were conducted, using samples A and B at different C rates of 0.1, 0.2, 0.5, and 1C (= 180 mA/g) between 3 and 4.5 V, using the same C rate for charging and discharging. Cathodes for battery test cells were made of the active material (~25 mg), super P carbon black (MMM, Belgium), and polyvinylidene fluoride (PVdF) binder (Kureha Company) in a weight ratio of 96:2:2. A cathode-slurry was prepared by thoroughly mixing a *N*-methyl-2-pyrrolidene (NMP)

solution with the PVdF, the carbon black, and the powdery cathode-active material. Electrodes were prepared by coating the cathode-slurry onto an Al foil, followed by drving at 130 °C for 20 min. Coin-type battery test cells (size 2016), containing a cathode, a Li metal anode, and a microporous polyethylene separator, were prepared in a helium-filled glove box. The electrolyte used was LiPF₆ with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (3/3/4 vol %) (Cheil Ind. Korea). After addition of the electrolyte, test cells were aged at room temperature for 24 h before electrochemical testing was performed. Field-emission transition electron microscopy (FE-TEM) (JEOL 2100F), operating at 200 kV was used for investigating the microstructure of the samples. The soft oxygen K-edge XAS measurements of bare, coated LiCoO₂, and LiCoPO₄ powder were performed on U7 beamline in the storage ring of 2.5 GeV with the ring current of 130-180 mA at Pohang Light Source (PLS).

3. Results and discussion

Fig. 1 shows a TEM image of precipitated $Co_3(PO_4)_2$ nanoparticles at pH 5 in distilled water. Nanoparticles were relatively well-dispersed without aggregation, with a particle size of 5 nm. XRD patterns of the bare (sample A) and LiCoPO₄ phase, grown in the surface of the LiCoO₂, (sample B) were nearly identical to each other without any secondary phases (see supporting information). Fig. 2a and b exhibit TEM images of the sample A, and the lattice fringe of layered $LiCoO_2$ (003), with a space R-3m, has very smooth particle surface morphology. However, the TEM images of the sample B (Fig. 2c and d) do not show the coating layer, and, instead, the lattice fringe of (311), corresponding to an olivine LiCoPO₄ phase, is clearly observed. This result indicates that Co₃(PO₄)₂ nanoparticles completely reacted with Li in LiCoO₂, forming Li- $CoPO_4$ and partial lithium-deficient Li_xCoO_2 , according to the following reaction:



Fig. 1. TEM image of Co₃(PO₄)₂ nanoparticles precipitated at pH 5.



Fig. 2. (a) and (b) TEM images of bare $LiCoO_2$ cathode particle (b is magnified image of a), (c) and (d) TEM images of $LiCoO_4$ phase formed in $LiCoO_2$ cathode particle (d is magnified image of c). (e) Oxygen K-edge X-ray absorption spectral comparison for bare and coated $LiCoO_2$.

 $2/3Co_3(PO_4)_2 + LiCoO_2 \rightarrow LiCoPO_4 + Li_xCoO_2.$

The approximate surface LiCoPO₄ layer thickness was \sim 7 nm. In the case of the AlPO₄ coating, it did not react with the bulk LiCoO₂ phase, and a coating layer, separate from the bulk phase, was formed after annealing at 700 °C [11].

Surface-sensitive oxygen K-edge soft X-ray absorption spectra (XAS) have been measured in a total electron yield mode in order to examine surface composition of the olivine LiCoPO₄, grown in LiCoO₂, in comparison to that of bare LiCoO₂, which in general can give structural information of $\leq \sim$ sub hundreds angstrom depth from the sample surface. As shown in Fig. 2e, olivine LiCoPO₄, grown in LiCoO₂, shows somewhat different spectral feature from bare LiCoO₂ in that weak peak features of oxygen in olivine LiCoPO₄ phase (denoted by arrows A, B, and C) could be observed together with oxygen ion of LiCoO₂. The evolution of pre-edge peak A for the olivine LiCoPO₄ is effectively observed with respect to that of LiCoO₂ phase. The peak A corresponds to oxygen ions bonded into divalent cobalt ion in the olivine LiCoPO₄ phase. The peaks B and C can be also observed weakly in the olivine LiCoPO₄, grown in LiCoO₂. The fact means both olivine LiCoPO₄ and LiCoO₂ phases coexists in the surface region of the olivine LiCoPO₄, grown in LiCoO₂, which supported the TEM result that the olivine LiCoPO₄ phase was formed on the surface of bare LiCoO₂.

XRD diffraction patterns of the bare (A) and LiCoPO₄ phase, grown in the surface of the LiCoO₂(B) were measured after charging to 4.5 V and storage for 5 h at 90 °C, as shown in Fig. 3. The XRD patterns did not show any secondary phases after storage at 90 °C, but the TEM image of sample A reveals the lattice fringe of a (222) Li_{x} Co_2O_4 spinel phase (Fd3m) on the surface of the particle. In addition, there was much surface roughness (see inserted figure in Fig. 4a), indicating that surface defects that developed during storage were significant. On the contrary, the lattice fringe of the olivine LiCoPO₄ phase of sample B (020) was clearly observed on the surface of the particle (Fig. 4b), indicating no phase transformation into the spinel phase. Such structural transformation and defects are accompanied by dissolution of Co ions from the structure, and the amount of Co dissolution from sample A at 900 ppm was 13 times higher than that of sample B. A charging voltage of 4.5 V led to more severe changes of the lattice constant, c, up to $\sim 3\%$ [7,8], and such an abrupt structural change was reported to induce electrochemical grinding between the particles, eventually resulting in Co dissolution and an increase in the interfacial resistance at 90 °C.

Fig. 5 shows voltage profiles of samples A and B between 3 and 4.5 V at various C rates from 0.1, 0.2, 0.5, and 1C up to 50 cycles (1C = 180 mA/g). The first discharge capacities of 186 and 189 mAh/g for samples A and B, respectively, were similar to each other. In the case of sample A, the first discharge capacity at the 1C rate was



Fig. 3. XRD patterns of bare and olivine LiCoPO₄ phase, grown in LiCoO₂, before charging, after charging to 4.5 V, and after storage at 90 °C for 5 h.



Fig. 4. TEM images of (a) $LiCoO_2$ cathode and (b) $LiCoPO_4$ phase formed in $LiCoO_2$ after charging to 4.5 V at 90 °C for 5 h. After charging the cell, electrode was separated from the cell and kept in the electrolytes in vials.

163 mAh/g, and it decreased to 84 mAh/g after 50 cycles. Sample B had a first discharge capacity of 171 mAh/g at the 1C rate and the discharge capacity after 50 cycles was 153 mAh/g, which is 45% higher than the bare sample. It is worth noting that the average voltage of the LiCoPO₄ phase, formed on LiCoO₂, was 0.2 V higher than the bare sample at 1C, indicative of the decreased overpotential, caused by the LiCoPO₄ formation. Such improvement is believed to be that the nanometer-scale olivine layer helps the electrical conduction due to the reduced the surface scattering that enhanced the total resistivity of the material [19].



Fig. 5. Plots of the coin-type half cells containing (a) bare and (b) $LiCoPO_4$ phase formed in $LiCoO_2$ cathode between 3 and 4.5 V at different C rates from 0.1 to 1C (1C = 18 mA/g). Same C rates were used during charge and discharge.

Fig. 6 shows changes in the thickness of the Li-ion cell, containing samples A and B that are stored at 4.4 V (vs. graphite) and 90 °C. This test is critical for checking the stability of the cathode in the cell at elevated temperatures, and Li-ion cell manufacturers require only 10% swelling at 90 °C after 5 h at 4.2 V. We found that both cell thicknesses, directly following charging to 4.4 V, were 4.7 mm, but the thickness of the cell containing bare cathode (sam-

ple A), rapidly increased to 7 mm after 5 h. On the other hand, the thickness of the cell containing the AlPO₄-coated cathode only increased to 6 mm, corresponding to a 50% increase. However, the cell containing sample B swelled only 10%, increasing to 4.9 mm, even after 11 h. This result indicates that the LiCoPO₄ phase, grown in LiCoO₂, effectively reduces electrolyte decomposition. As discussed in the introduction, for the AlPO₄-coated sample, residual amounts of LiOH and Li₂CO₃ in the annealed sample, corresponding to 150 and 250 ppm, respectively, were observed. On the other hand, amounts of these impurities in the LiCoPO₄ grown in LiCoO₂ were negligible. We believe that these impurity phases decomposed into hydrogen and CO₂ gas at 90 °C.

Fig. 7 shows plots of the cell surface temperature of the Li-ion cells, containing samples A and B, after nail penetration testing at 4.4 V. The first case (bare cell) showed a maximum cell surface temperature above 500 °C, and the inserted figure shows the cell appearance after the test. A maximum surface temperature above 500 °C was observed in the cell containing bare sample A, along with sparks and fire, while the cell with sample B showed a maximum temperature of 80 °C without thermal runaway. This indicates that the LiCoPO₄ phase reduced exothermic reactions with the electrolytes.

In conclusion, the olivine LiCoPO₄ phase, grown in the LiCoO₂ cathode by nanoparticle $Co_3(PO_4)_2$ coating, exhibited not only excellent electrochemical properties, but also showed good structural integrity at 90 °C and under thermal abuse testing. In addition, this coating process also scales-up easily and does not require anti-fire facilities since water is used as the solvent for nanoparticle precipitation and coating.



Fig. 6. Plot of the cell thickness change at 4.4 V during storage at 90 °C out to 5 h using bare $LiCoO_2$ (sample A), $LiCoPO_4$ phase formed in $LiCoO_2$ (sample B), and AlPO₄-coated $LiCoO_2$. Inserted photographs are of cell morphology after charging and after finishing swelling test.



Fig. 7. Plot of cell surface temperatures after nail penetration of the Li-ion cells containing bare $LiCoO_2$ (sample A), $LiCoPO_4$ phase formed in $LiCoO_2$ (sample B). Inserted photographs are of cell morphology after tests. Bare cell were stained with soot.

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References

- Annual Report on Advanced Rechargeable Battery Industry in 2005, Nomura Research Institute Ltd., Japan, 2006.
- [2] S.B. Schougaard, J. Breger, M. Jiang, C.P. Grey, J.B. Goodenough, Adv. Mater. 18 (2006) 905.
- [3] J. Choi, A. Manthiram, Electrochem. Solid State Lett. 8 (2005) C102.
- [4] G.-H. Kim, S.T. Myung, H.J. Bang, J. Prakash, Y.-K. Sun, Electrochem. Solid State Lett. 7 (2004) A477.
- [5] H. Omanda, T. Brousse, C. Marhic, D.M. Schleich, J. Electrochem. Soc. 151 (2004) A922.
- [6] J. Cho, Chem. Mater 13 (2001) 4537.
- [7] Y.-I. Jang, N.J. Dudney, D.A. Blom, L.F. Allard, J. Electrochem. Soc. 149 (2002) A1442.

- [8] G.G. Amatucci, J.M. Tarascon, L.C. Klein, Solid State Ionics 83 (1996) 167.
- [9] J. Cho, Y.J. Kim, T.-J. Kim, B. Park, Angew. Chem. Int. Ed. 40 (2001) 3367.
- [10] J. Cho, Y.J. Kim, B. Park, Chem. Mater. 12 (2000) 3788.
- [11] J. Cho, J.-G. Lee, B. Kim, B. Park, Chem. Mater. 15 (2003) 3190.
- [12] J. Cho, Y.J. Kim, B. Park, J. Electrochem. Soc. 148 (2001) A1110.
- [13] J. Cho, Y.-W. Kim, B. Kim, J.-G. Lee, B. Park, Angew. Chem. Int. Ed. 42 (2003) 1618.
- [14] Y.J. Kim, H. Kim, B. Kim, D. Ahn, J.-G. Lee, T.-J. Kim, D. Son, J. Cho, Y.-W. Kim, B. Park, Chem. Mater. 15 (2003) 1505.
- [15] J. Cho, J.-G. Lee, B. Kim, T.-G. Kim, B. Park, J. Power Sources 50 (2005) 4182.
- [16] J. Kim, Y. Hong, K.S. Ryu, M.G. Kim, J. Cho, Electrochem. Solid State Lett. 9 (2006) A19.
- [17] K. Amine, H. Yasuda, M. Yamachi, Electrochem. Solid State Lett. 3 (2000) 178.
- [18] A.K. Padhi, K. Nanjundaswamy, A. Manthiram, J.B. Goodenough, J. Electrochem. Soc. 44 (1997) 1188.
- [19] G. Cao (Ed.), Nanostructures and Nanomaterials, World Science Publishing Co. Ltd., Singapore, 2004.